AD-752 564

RATES AND MECHANISMS OF REACTIONS OF FLUORINE CONTAINING ROCKET PROPELLANTS

Thomas Houser

Western Michigan University

AD752564

RATES AND MECHANISMS OF REACTIONS
OF FLUORINE CONTAINING
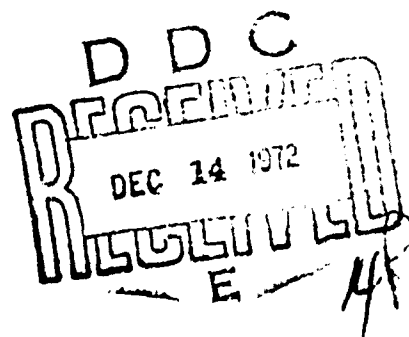ROCKET PROPELLANTS

Prepared by: Thomas Houser

October 1972

Research Sponsored by

Air Force Office of Scientific Research
~~Office of Aerospace Research~~
United States Air Force

Approved for Public Release: Distribution Unlimited

Chemistry Department
Western Michigan University
Kalamazoo, Michigan 49001

D D C
DEC 14 1972
E

"Qualified requestors may obtain additional copies from the Defense Documentation Center, all others should apply to the Clearinghouse for Federal Scientific and Technical Information"

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
WESTERN MICHIGAN UNIVERSITY CHEMISTRY DEPARTMENT KALAMAZOO, MICHIGAN 49001	UNCLASSIFIED
	2b. GROUP

3. REPORT TITLE

RATES AND MECHANISMS OF REACTIONS OF FLUORINE CONTAINING ROCKET PROPELLANTS

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Scientific   Interim

5. AUTHOR(S) *(First name, middle initial, last name)*

THOMAS HOUSER

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
October 1972	11	12

8a. CONTRACT OR GRANT NO. AFOSR-72-2160	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO. 9750-02	
c. 61102F	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d. 681308	AFOSR-TR-72-2028

10. DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
TECH, OTHER	AF Office of Scientific Research (NAE) 1400 Wilson Boulevard Arlington, VA 22209

13. ABSTRACT

The suitability of the mechanism proposed by Prof. H. J. Schumacher to describe the kinetic data for the pyrolysis of OF_2 was discussed. In view of its limitations, an alternate mechanism was proposed, which is consistent with all of the most recent kinetic data. The study of the rate of the H_2-OF_2 reaction was continued in a magnesium reactor in an attempt to further reduce the surface effects. The indications are that the heterogeneous contributions to the rate are less than those found in monel or aluminum. A mechanism was proposed to explain the rate data obtained in the aluminum reactor. Up to the present time it has not been possible to obtain reproducible kinetic data for the oxygen inhibited H_2-N_2F_4 reaction.

$\mathcal{I}$

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
OXYGEN DIFLUORIDE						
TETRAFLUOROHYDRAZINE						
GAS PHASE KINETICS						
FLOW SYSTEM KINETICS						
REACTION RATES						
IGNITION RATES						
REACTION MECHANISMS						
FLUORINE CONTAINING OXIDIZERS						

RATES AND MECHANISMS OF REACTIONS
OF FLUORINE CONTAINING
ROCKET PROPELLANTS

Prepared by
Thomas Houser
October 1972

Interim Scientific Report
Grant No. ⬤AFOSR-72-2160
Period Covered: 1 September 1971 - 31 August 1972

Research Sponsored
By
Air Force Office of Scientific Research
~~Office of Aerospace Research~~
United States Air Force

Approved for public release; Distribution unlimited

<u>Conditions of Reproduction</u>

Reproduction, translation, publication, use and disposal in whole or in
in part by or for the United States Government is permitted

Chemistry Department
Western Michigan University
Kalamazoo, Michigan 49001

II

CONTENTS

INTRODUCTION

OBJECTIVE

The objective of this study is to obtain a better understanding of the chemical properties of fluorine containing rocket propellants. The compounds selected for study were OF_2 and N_2F_4 because their chemical properties have not been well established. Furthermore, they contain groups which contribute to the composition of many new high energy propellants; thus, a knowledge of their reaction mechanisms will contribute to the understanding of the chemical behavior of many new propellants. This report describes the progress made on this study during the period 1 October 1971 to 30 September 1972.

PREVIOUS RESULTS

The problems associated with obtaining and understanding the pyrolysis kinetics and mechanism of OF_2 were described in detail in last year's report.[1] The results presented in that report, and those obtained in the most recent investigations,[2-4] indicate that the reaction probably proceeds by a chain mechanism of very short length. However, the exact nature of this mechanism is still a source of controversy; the pertinent arguments will be discussed in the section on current results.

The kinetics of the H_2-OF_2 reaction had not been reported previous to the results of this program.[1,5] It is apparent that this reaction has a large heterogeneous contribution when carried out in monel or aluminum reactors, and that the mechanism is extremely complex. Work is continuing to find reactor materials which will reduce surface

effects and to formulate mechanisms consistent with the kinetic data.

It was found that there was a similar lack of kinetic data for the H_2-N_2F_4 reaction. A mechanism for the explosive reaction between these two compounds has been postulated,[6] based on product distribution data. However, kinetic data have not been obtained to substantiate the mechanism.

EXPERIMENTAL TECHNIQUES

A complete description of the apparatus and procedure was reported previously.[1] The following is a brief outline of the experimental techniques employed to obtain the kinetic data.

A stirred-flow reactor has been used because it is possible to get differential rate data directly according to the equation

$$rate = (c_o - c)/t_c$$

where c_o and c are the reactant concentrations entering and leaving the reactor respectively and t_c is the contact time (reactor volume/volume rate of flow). The advantage of differential rate data is that it allows the elucidation of complex rate equations more easily.

The rate was determined by measuring the reactant concentrations mass spectrometrically. Since the flow system was operated at atmospheric pressure, it was necessary to equip the mass spectrometer with an atmospheric sampler for the continuous monitoring of the concentrations entering and leaving the reactor. The flow rates were measured using calibrated capillary flow meters. The reactants were stored under pressure in tanks at the appropriate partial pressures (helium was used as the diluent) to give the desired concentrations.

DISCUSSION OF CURRENT RESULTS

PYROLYSIS OF OF_2

Because of the difference in interpretation of the most recent OF_2 pyrolysis data between Prof. H. J. Schumacher and this investigator,[4] it appears that a discussion of some of the considerations involved would be worthwhile.

It is believed that the data reported by Prof. Schumacher[4] using a static system and pressure rise measurements, and that obtained from this program in a flow system are mutually consistent, and are different from that reported in all other previous studies.[2,7-12] These previous studies found that the kinetic data were consistent with a first-order rate equation (all involved mixtures of OF_2 and diluent) and the first-order constant was directly proportional to total pressure. However, the data from this program indicated that for OF_2-helium mixtures the rate was somewhat less than first-order in (OF_2) (it was reasonably well established that the reaction is not heterogeneous), consistent with the equation
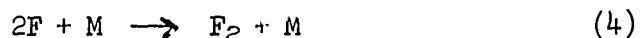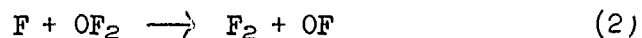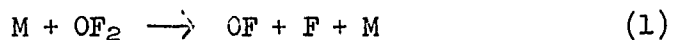
$$\text{rate} = k_a(OF_2)M + k_b(OF_2)^{1/2}M \qquad (A)$$

where M = concentration of diluent gas. Similarly, Professor Schumacher's results with neat OF_2 indicated a rate somewhat less than second-order, consistent with the equation

$$\text{rate} = k_a'(OF_2)^2 + k_b'(OF_2)^{3/2} \qquad (B)$$

It can be seen that these equations are identical if the M in equation A is replaced by (OF_2).

Although it is possible to consider these equations identical, different mechanisms can be propsed to account for them. Professor Schumacher has proposed the following mechanism:

$$M + OF_2 \longrightarrow OF + F + M \tag{1}$$

$$F + OF_2 \longrightarrow F_2 + OF \tag{2}$$

$$2OF \longrightarrow O_2 + 2F \tag{3}$$

$$2F + M \longrightarrow F_2 + M \tag{4}$$

the steady-state treatment of which leads to the rate equation

$$\text{rate} = k_1(OF_2)M + k_2(k_1/k_4)^{1/2}(OF_2)^{3/2} \tag{C}$$

Both equations A and C are intended to describe the reaction involving inert diluent as the energizing species and these equations are not identical, however, if M in equation C is replaced by (OF_2), equations B and C are the same.

An alternate mechanism can be propsed which is consistent with both equations A and B. If steps 3 and 4 are replaced by the following

$$OF + M \longrightarrow O + F + M \tag{5}$$

$$2OF + M \longrightarrow O_2 + F_2 + M \tag{6}$$
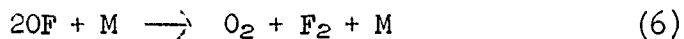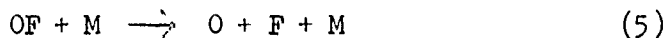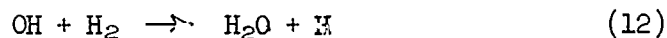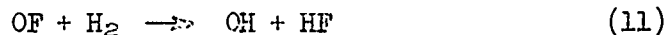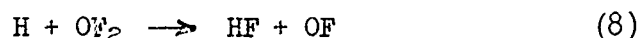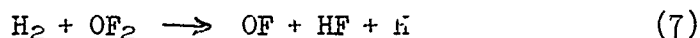
the steady-state treatment will yield equation D

$$\text{rate} = 2k_1(OF_2)M + k_5(k_1/k_6)^{1/2}(OF_2)^{1/2}M \tag{D}$$

which is identical to equation A. It can be concluded that a mechanism consisting of steps 1,2,5 and 6 will explain both experimental rate equations, while the other combination of steps (utilizing 3 and 4) accounts only for equation B. Unequivocal verification of which mechanism is applicable can be obtained by determining the order of the pyrolysis with respect to (OF_2) in a static system when the reactant is highly diluted. This was not done by Professor Schumacher, presumably because of the large uncertainties in results from pressure rise systems under these conditions. Thus, it is necessary to use an analytical technique which will measure the OF_2 concentration directly, e.g. mass spectrometry.

H_2-OF_2 REACTION

The study of the rate of this reaction showed that in a monel reactor there was a significant surface effect.[1,5] In an attempt to reduce the heterogeneity of the reaction, aluminum and magnesium were used as reactor materials. Two observations from the experiments in the aluminum reactor indicated that the heterogeneous contributions to the rate of the oxygen inhibited reaction had been reduced when compared to those obtained in monel: (a) increasing the surface area increased the rate by a smaller amount, and (b) higher temperatures were necessary to obtain comparable extents of reaction, other conditions being equal.

Because the rate data from the aluminum reactor lead to unusual concentration dependencies, orders of about 1.25 and 0.25 for OF_2 and H_2 respectively, it was interesting to see what type of mechanism could be applicable. The following reaction scheme is proposed as a possible mechanism for the oxygen inhibited reaction.

$$H_2 + OF_2 \longrightarrow OF + HF + H \tag{7}$$

$$H + OF_2 \longrightarrow HF + OF \tag{8}$$

$$2OF \longrightarrow O_2 + 2F \tag{9}$$

$$F + H_2 \longrightarrow HF + H \tag{10}$$

$$OF + H_2 \longrightarrow OH + HF \tag{11}$$

$$OH + H_2 \longrightarrow H_2O + H \tag{12}$$

$$H + O_2 + M \longrightarrow HO_2 + M \tag{13}$$

$$F + HO_2 \longrightarrow HF + O_2 \tag{14}$$

$$2H + M \longrightarrow H_2 + M \tag{15}$$
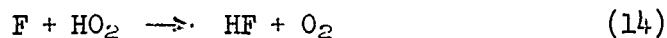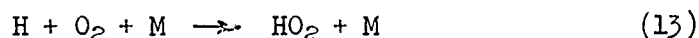
The steady-state treatment of this mechanism yields the equation

$$rate = k_7(OF_2)(H_2) + k_8 k_7(OF_2)^2(H_2)/k_{13}(O_2)M$$

$$-k_7{}^2 k_{15}(OF_2)^3(H_2)^2/k_{13}{}^3(O_2)^3 M^2 \tag{E}$$

However, it was necessary to use a series expansion of the root of the
quadratic solution for the steady-state H atom concentration and use
only the first three terms, which introduces an error in (H) of less
than 3%. Plots of rate/$(OF_2)^2(H_2)$ vs. $(OF_2)(H_2)$ using the data from the
aluminum reactor (which assumes that the initiation rate is negligible)
are consistent with equation E. Other mechanisms did not fit the data
as well.

Work has just begun in the magnesium reactor, but again a tem-
perature increase is necessary to achieve reasonable extents of re-
action, indicating another reduction in surface contributions to the

rate. Because of the higher temperatures necessary, it is believed that initiation could start with O_2 pyrolysis and would not require inter- action with H_2. Thus the reaction order may be significantly different in the magnesium reactor.

H_2-N_2F_4 REACTION

Because of the inability to obtain a controlled reaction with dilute mixtures of these reactants, due to a series of minature explosions dur- ing the flow experiment, oxygen was added as an inhibitor. Under these conditions a controlled, steady-state reaction was achieved. However, the apparent rate data were not reproducible, i.e. the extent of re- action continually decreased in successive experiments, although steady-state reactant concentrations were obtained during a given run. Thus, meaningful kinetic data have not been obtained as yet. The in- fluence of impurities on the irreproducibility of the reaction rate is being investigated.

REFERENCES

1. T. J. Houser, "Rates and Mechanisms of Reactions of Fluorine Containing Rocket Propellants," Air Force Office of Scientific Research, AFOSR, TR-71-2993, Nov. 1971.

2. W. C. Solomon, J. A. Blauer and F. C. Jaye, J. Phys. Chem., 72, 2311 (1968).

3. T. J. Houser and T. W. Asmus, J. Am. Chem. Soc., 94, 3326 (1972).

4. H. J. Schumacher, "13th AFOSR Contractors' Meeting on Kinetics of Energy Conversion," September 1972.

5. T. W. Asmus and T. J. Houser, Inorg. Chem., 11, 234 (1972).

6. L. P. Kuhn and C. Wellman, Inorg. Chem., 9, 602 (1970).

7. L. Dauerman, G. E. Salser and Y. A. Tajima, J. Phys. Chem., 71, 3999 (1967).

8. J. Troe, H. G. Wagner. and G. Weden, Z. Phys. Chem. (Frankfort am Main), 56, 258 (1967).

9. J. A. Blauer, and W. C. Solomon, J. Phys. Chem., 72, 2307 (1968).

10. M. C. Lin and S. H. Bauer, J. Am. Chem. Soc., 91, 7737 (1969).

11. H. Henrici, M. C. Lin and S. H. Bauer, J. Chem. Phys., 52, 5834 (1970).

12. W. Koblitz and H. J. Schumacher, Z. Phys. Chem. (Leipzig), B25, 283 (1934).